Optical Engineering 45(12), 123801 (December 2006)

Investigation of the optical properties of sputtered ZnO films by reflectance spectroscopy

Bo Huang
Jing Li
Dong-hui Guo
Xiamen University
Physics Department
Xiamen 361005, China

Sun-tao Wu
Xiamen University
Pen-Tung Sah MEMS Research Center
Xiamen 361005, China
E-mail: wst@xmu.edu.cn

Abstract. ZnO films have been deposited on SiO_2/Si substrates by rf magnetron sputtering. The rms roughness of the sample's surface was surveyed by using an atomic force microscope, and is less than 10 nm. The theoretical reflectance of the air/film/middle layer/substrate structure has been deduced. In the light of this theoretical reflectance, the complex refractive index $\tilde{n}(\lambda)=n(\lambda)+ik(\lambda)$ of the sample below the interband absorption edge has been fitted with a Lorentz oscillator model. The absorption coefficient $\alpha(\lambda)$ of the sample is reported, and the result shows the sample has weak absorption around 490 nm. [DOI: 10.1117/1.2402102]

Subject terms: zinc oxide; spectroscopy; AFM.

Paper 051005R received Dec. 23, 2005; revised manuscript received Mar. 24, 2006; accepted for publication May 23, 2006; published online Dec. 26, 2006.

1 Introduction

Zinc oxide film has drawn much interest as a potential transparent conducting oxide (TCO) for applications in solar cells and optoelectronic devices, due to its advantages of nontoxicity, low cost, and abundance as a raw material.[1–3] In view of these applications, there is a need for accurate data on the optical properties of ZnO films over a wide wavelength range. Although the optical constants of bulk ZnO crystal have been measured by Yoshikawa and Adachi using spectroscopic ellipsometry,[4] this powerful technique displays extreme surface sensitivity that limits its application to ZnO films, since their optical properties are dependent on deposition conditions and preparation methods. The other most commonly used techniques to determine the optical constants involve measuring the normal-incidence transmission coefficient T and/or the near-normal-incidence reflection coefficient R. However, only the reflectivity can be measured for a film deposited on an opaque substrate. Reference 5 gives a critical review of the advantages and disadvantages of these and other important methods.

But those methods cannot be used directly to study the optical properties of ZnO films, for the following reasons:

1. As the TCO for applications in solar cells or optoelectronic devices, usually, ZnO film is deposited on an opaque substrate, so that transmission measurements methods cannot be used.[6]
2. When using reflectance data only, one can only deal with an air/film/substrate structure,[7,8] whereas in practice ZnO films are often used on air/ZnO film/middle-layer/substrate multilayer structures. More complex formulas and different boundary conditions must be used to describe such a structure's reflectance.
3. Some of the methods are too complex or lack a direct physical interpretation.[9,10]

In the present paper sputtered ZnO films with smooth surfaces, which have only a tiny absorption in the visible region, are surveyed. A theoretical expression for the reflectance of an air/film/middle-layer/substrate structure as a function of wavelength is deduced. The optical dispersion below the interband absorption edge has been fitted with a Lorentz oscillator model based on the theoretical reflectance. The complex refractive index $\tilde{n}(\lambda)=n(\lambda)+ik(\lambda)$ of the ZnO film is estimated from the spectrum of near-normal reflection in the light of the preceding models. We demonstrate that fitting of the reflection spectra below the near-band-edge absorption region becomes possible, allowing the determination of the film thickness, complex refractive index $\tilde{n}(\lambda)=n(\lambda)+ik(\lambda)$, and absorption coefficient $\alpha(\lambda)$ for films deposited under appropriate conditions.

2 Experimental Procedure

A silicon substrate was cleaned by the standard cleaning process, and a SiO_2 layer was prepared by the thermal oxidative technique. The substrate was then segmented into four small samples with size 2.0×2.5 cm. This procedure was adopted to minimize the effect of the SiO_2 layer on the reflection spectrum measurement, and the SiO_2 thickness can be used as a parameter to evaluate the fitting results, for the fitted SiO_2 thickness should have the same value. Then ZnO films were deposited on these $SiO_2/Si(100)$ substrates by rf magnetron sputtering using a ZnO target (99.99%) in a gas mixture of Ar (99.99%) and O_2 (99.99%) with different $Ar:O_2$ ratios: 0, 1:4, 2:3, and 4:5. These samples are labeled R1, R2, R3, and R4, respectively. During film deposition, the rf power was 75 W, and the total pressure was maintained at 1 Pa. The substrate temperature was kept at 200 °C. The sputtering time was 60 min.

The reflection spectra of the samples were measured

0091-3286/2006/$22.00 © 2006 SPIE

with a Varian Cary-300 spectrophotometer within the range from 350 to 800 nm at room temperature in air. The samples' thickness was measured with a Sloan Dektak3 surface profilometer, and it was noted that each sample was of uniform thickness. Sample surface morphologies were investigated with an AJ-III atomic force microscope (AFM).

3 Theoretical Model

In this section we firstly deduce the theoretical reflectance of the air/film/middle-layer/substrate structure. Let the layers be labeled with the numbers 0, 1, 2, and 3, respectively, and the light be incident normally from the air side. The reflected energy is given by[9]

$$R(\lambda) = \left| \frac{M_{21}}{M_{22}} \right|^2, \tag{1}$$

where

$$M = S_3 K_2 S_2 K_1 S_1, \tag{2}$$

$$K_i = \begin{bmatrix} \exp(-i2\pi\tilde{n}_i d_i/\lambda) & 0 \\ 0 & \exp(i2\pi\tilde{n}_i d_i/\lambda) \end{bmatrix}, \tag{3}$$

$$S_i = \frac{1}{2\tilde{n}_i} \begin{bmatrix} \tilde{n}_i + \tilde{n}_{i-1} & \tilde{n}_i - \tilde{n}_{i-1} \\ \tilde{n}_i - \tilde{n}_{i-1} & \tilde{n}_i + \tilde{n}_{i-1} \end{bmatrix}, \tag{4}$$

where $\tilde{n}_i$ is the complex refractive index of layer i, and d_i is its thickness. The matrix S_i characterizes the light transmission between the interface of layers i and $i-1$. The matrix K_i describes the phase shift and attenuation of light passing through layer i. The quantities M_{21} and M_{22} are then elements of the matrix M. Because the narrow band gap of the Si substrate, the back surface reflection from the interface between Si and air is completely inhibited, so the subscript of S_i is less than 3. Due to their compact matrix form, these formulas are suitable for computer processing even though the resulting formula for the reflectivity is an intricate one.

It is well know that estimating the thickness and the optical constants of thin films from the spectrum of reflectance is a highly underdetermined optimization problem. Numerous methods have been devised to solve the problem.[7,9] The most practical method assumes a specific empirical dispersion equation for the wavelength-dependent complex refractive index. The equations used most often are those of the Lorentz classical oscillator model:[11]

$$\begin{aligned} n^2 - k^2 &= \epsilon_0 + \frac{A\lambda^2}{\lambda^2 - \lambda_0^2 + \gamma\lambda^2/(\lambda^2 - \lambda_0^2)}, \\ 2nk &= \frac{A\gamma^{1/2}\lambda^3}{(\lambda^2 - \lambda_0^2)^2 + \gamma\lambda^2} \end{aligned} \tag{5}$$

with λ_0 the oscillator central wavelength, A the oscillator strength, and γ the damping factor; ϵ_0 is the dielectric function at wavelengths much smaller than the measured one. Equation (5) describes the dispersion relations below the interband absorption edge in ionic materials very well.[12] So we fit the reflectance spectroscopy data from 400 to 800 nm using the dispersion equation (5).

In order to get the complex refractive index of Si, we measure the reflectivity of the substrate alone and perform exact fitting. Based on the fitting results, the parameters of SiO_2 are deduced from the reflectivity of the SiO_2/Si system. The fitting results for the refractive indices of SiO_2 and Si are

$$n_{SiO_2}(\lambda) = \left(1 + \frac{1.085\lambda^2}{\lambda^2 - 8457}\right)^{1/2}, \tag{6}$$

$$n_{Si}(\lambda) = 6.114 - \frac{3500}{\lambda} + \frac{1.298^6}{\lambda^2}, \tag{7}$$

$$k_{Si}(\lambda) = 0.905 - \frac{1169}{\lambda} + \frac{3.785^5}{\lambda^2}. \tag{8}$$

Based on the preceding discussion, the parameters in the dispersion equations are determined using a least-squares fitting procedure. It is common to include the thickness of the ZnO film and the SiO_2 layer as fitting parameters. But so many fitting parameters often lead to an ill-conditioned Jacobian determinant, so we firstly fixed the ZnO film and SiO_2 layer thickness at values determined by a surface profilometer. Earlier reports have indicated that sputtered ZnO films often exhibit an broad deep level emission around 490 to 510 nm.[13–16] Even though the exact origin of the defects centers is still debatable, it is reasonable to assign 500 nm as the initial value of the oscillator center wavelength. After the oscillator strength A and the damping factor γ are derived, all these parameters are fitted again. The results should have values close to the SiO_2 layer thickness, because all the films were deposited on the same substrate. The results should confirm that the ZnO film thickness increases with the increasing Ar/O_2 ratio because argon has a higher sputtering yield than oxygen, as is verified by the surface profilometer.

4 Results and Discussion

4.1 *Reflection Spectrum Measurement*

The applicability of a fitting model is guaranteed if there is a good fit between the experimental reflection spectrum and the one calculated from the theoretical reflectance using the dispersion equation, but we must ensure that the experimental data are not corrupted by other factors. Roughness of the films produces disproportionate changes in reflectivity for different incident wavelengths,[17] so samples with smooth surfaces and near-normal reflectance spectra are used to validate the preceding model. The incidence angle is less than 5 deg in the reflection measurement.

AFM images of the samples surface are shown in Fig. 1. The rms roughness does not show any distinct dependence on the sputtering ambience and is less than 10 nm; however, the grain size seems to grow with increasing Ar/O_2 ratio: see Table 1.

The reflection spectra of the samples are shown in Fig. 2. For all samples, these have a near-band-edge absorption in the range of 370 to 400 nm. The interference fringes between 400 and 800 nm are due to the multiple reflection

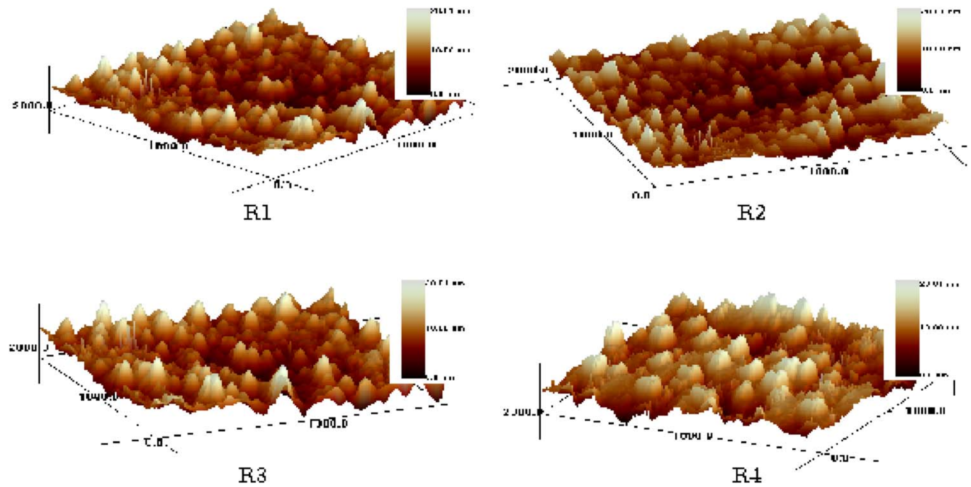

Fig. 1 AFM image of the sample surfaces with scan size 2×2 μm and vertical scale 0 to 20 nm.

between the ZnO film and the substrate, similar to Fabry-Perot reflection. All samples have a maximum reflectivity in the range of 450 to 550 nm, which indicates that these samples have absorption in the range of 450 to 550 nm. The fitting results for the absorption coefficient also confirm this; see Fig. 4.

4.2 *Computational Results*

Figure 3 shows the fitting results for sample R3. Noted that the fitting data agree well with the true data from 400 to 800 nm, but below 400 nm the fitting result does not coincide with the experimental data, because the single-oscillator model cannot characterize the strong absorption near the band edge. Other samples yield similar results. The fitted refractive index at 600 nm can be found in Table 1; it is less than the value given in Ref. 4, since the sputtered ZnO films contain voids that will reduce the refractive index from that of a ZnO crystal.

From the fitting result, we can deduce the absorption coefficient $\alpha(\lambda)$. It is shown in Fig. 4. We can find that samples R3 and R4 have smaller absorption coefficients than samples R1 and R2. This may be understood from the fact that the ambience with less oxygen would induce more oxygen vacancies than had been assumed, and those defect states lead to absorption around 500 nm.[14,16] All the fitting parameters of the Lorentz oscillator model can be found in Table 1. The fitted thickness of the ZnO films, d_{ZnO}, is close to the true value measured by the surface profilometer.

4.3 *Effect of Sample Surface*

A general method to estimate the thickness and the optical constants of thin films using reflectance data only would be a huge mathematical challenge. We only consider the energy range from 400 to 800 nm, which is below the energy band gap of ZnO, because when a full energy range is included one needs local (nonglobal) solutions and a more complex dispersion model must be adopted. To cover a full energy range, one usually introduces piecewise dispersion relations.[7] Because our samples are polycrystal films, the optical properties below the interband absorption edge are most significant, so we only inspect the reflectance spectroscopy data from 400 to 800 nm using a common dispersion equation (5). Our method is suitable only for samples with smooth surfaces and with interference fringes in the reflection spectrum, because surface roughness would cause the reflectance to vary with wavelength, and we must keep this variation as small as possible within the range from 400 to 800 nm.

The reflectivity R of a film with rms roughness δ is given by[17]

Table 1 The structural properties and fiting parameters of Lorentz model for ZnO films.

Sample	ϵ_0	λ_0 (nm)	A	γ (10^{-5} nm^2)	Fitted d_{ZnO} (nm)	True d_{ZnO} (nm)	Fitted $d_{\mathrm{SiO_2}}$ (nm)	n at 600 nm	Rms roughness (nm)	Grain size (nm)
R1	2.91	489	0.450	2.44	305	299	289	1.83	8.1	7–12
R2	3.55	496	0.307	1.13	315	318	295	1.83	2.5	7–12
R3	2.89	488	0.220	0.916	393	401	292	1.84	3.4	16–25
R4	2.92	486	0.270	1.36	412	421	303	1.83	6.6	35–55

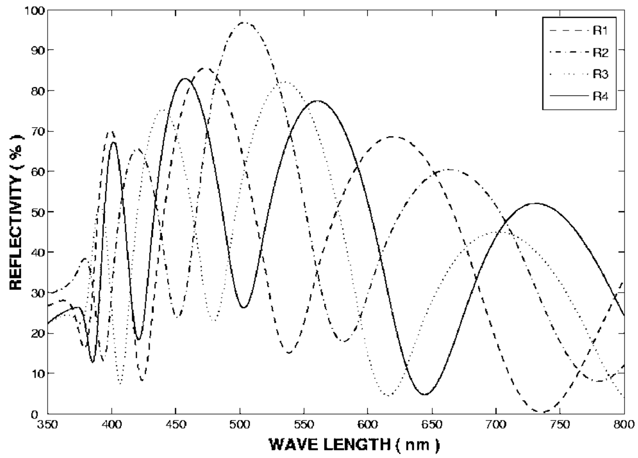

Fig. 2 The reflection spectra of samples R1, R2, R3, R4.

$$R = R_0 \exp\left(-\frac{16\pi^2\delta^2}{\lambda^2}\right), \tag{9}$$

where R_0 denotes the reflectivity of the sample without roughness. From Eq. (9) we obtain

$$\delta = \left[\frac{\ln(R_1/R_2)}{16\pi^2(\lambda_2^{-2} - \lambda_1^{-2})}\right]^{1/2}. \tag{10}$$

From Eq. (10) we can estimate the valid range of rms roughness for our method. In our fitting range 400 to 800 nm, the variation of the reflection coefficient due to surface roughness is below 5% for rms roughnesses less than 8 nm. Larger rms roughness will invalidate this method if the samples are deposited with large power. In our experimental conditions, a power lower 120 W is recommended.

5 Conclusion

The optical properties of ZnO films with smooth surfaces deposited on SiO_2/Si substrates have been investigated using reflectance measurements in the spectral range of 400 to 800 nm at room temperature. For samples with smooth surfaces, we can fit the near-normal reflection spectra with a simple, physically straightforward model. The results show these samples have a weak absorption around 490 nm.

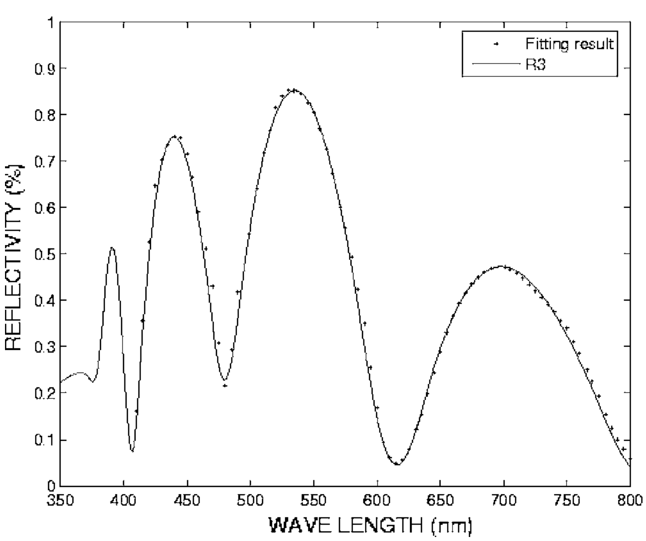

Fig. 3 True and fitted reflection spectra of sample R3.

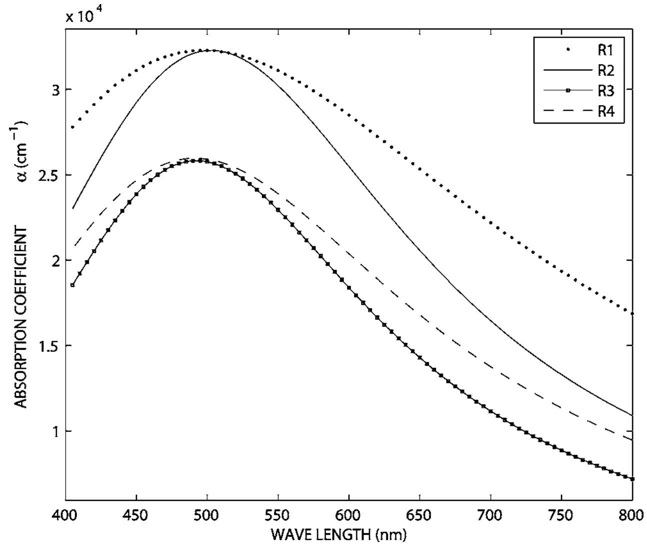

Fig. 4 The absorption coefficients $\alpha(\lambda)$ of samples R1, R2, R3, R4.

Acknowledgments

This work was financially supported by the Ministry of Science and Technology of China (No. 2001CB610506), the Natural Science Foundation of China (No. 90206039), and the Science and Technology Project of Fujian province of China (No. 2005H043)

References

1. G. Gordillo and C. Calderón, "Properties of ZnO thin films prepared by reactive evaporation," *Sol. Energy Mater. Sol. Cells* **69**, 251–260 (2001).
2. R. Schäffler and H. W. Schock, "High mobility ZnO:Al thin films grown by reactive dc magnetron sputtering," in *Conf. Record of the Twenty-Third IEEE Photovoltaic Specialists Conf.*, pp. 1026–1030 (1993).
3. J. M. Bian, X. M. Li, X. D. Gao, W. D. Yu, and L. D. Chen, "Deposition and electrical properties of N–In codoped P-type ZnO films by ultrasonic spray pyrolysis," *Appl. Phys. Lett.* **84**(4), 541–543 (2004).
4. H. Yoshikawa and S. Adachi, "Optical constants of ZnO," *Jpn. J. Appl. Phys., Part 1* **36**, 6237–6243 (1997).
5. D. Poelman and P. F. Smet, "Methods for the determination of the optical constants of thin films from single transmission measurements: a critical review," *J. Phys. D* **36**, 1850–1857 (2003).
6. R. Swanepoel, "Determination of surface roughness and optical constants of inhomogeneous amorphous silicon films," *J. Phys. E* **17**, 896–903 (1984).
7. S. D. Ventura, E. G. Birgin, J. M. Martinez, and I. Chambouleyron, "Optimization techniques for the estimation of the thickness and the optical parameters of thin films using reflectance data," *J. Appl. Phys.* **97**(4), 043512(1–3) (2005).
8. S. Shokhovets, R. Goldhahn, V. Cimalla, T. S. Cheng, and C. T. Foxon, "Reflectivity study of hexagonal GaN films grown on GaAs: surface roughness, interface layer, and refractive index," *J. Appl. Phys.* **84**(3), 1561–1566 (1998).
9. E. G. Birgin, I. E. Chambouleyron, and J. M. Martinez, "Optimization problems in the estimation of parameters of thin films and the elimination of the influence of the substrate," *J. Comput. Appl. Mech.* **152**, 35–50 (2003).
10. W. E. Tennant and J. A. Cape, "Study of the dielectric function of PbSnTe epitaxial film by far-infrared reflectivity," *Phys. Rev. B* **13**(6), 2540–2547 (1976).

11. G. Martinez (Ed.), *Optical Properties of Semiconductors*, Kluwer Academic Publishers (1993).
12. S. H. Wemple and M. DiDomenico, Jr., "Behavior of the electronic dielectric constant in covalent and ionic materials," *Phys. Rev. B* **3**(4), 1338–1351 (1971).
13. K. Vanheusden, C. H. Seager, W. L. Warren, D. R. Tallant, and J. A. Voigt, "Correlation between photoluminescence and oxygen vacancies in ZnO phosphors," *Appl. Phys. Lett.* **68**(3), 403–405 (1996).
14. B. Lin, Z. Fu, and Y. Jia, "Green luminescent center in undoped zinc oxide films deposited on silicon substrates," *Appl. Phys. Lett.* **79**(7), 943–945 (2001).
15. D. H. Zhang, Z. Y. Xue, and Q. P. Wang, "The mechanisms of blue emission from ZnO films deposited on glass substrate by r.f. magnetron sputtering," *J. Phys. D* **35**, 2837–2840 (2002).
16. P.-S. Xu, Y.-M. Sun, C.-S. Shi, F.-Q. Xu, and H.-B. Pan, "Native point defect states in ZnO," *Chin. Phys. Lett.* **18**(9), 1252–1253 (2001).
17. I. Ohlídal, F. Lukeš, and K. Navrátil, "Rough silicon surfaces studied by optical methods," *Surf. Sci.* **45**, 91–116 (1974).

Bo Huang received his diploma in physics from Xiamen University, China, in 1998. He is currently a PhD student in the Physics Department there. His research work focuses on developing new nanometer-scale materials with novel properties, and optoelectronic materials and devices.

Biographies and photographs of the other authors not available.